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"Palladium in Non-Aqueous Solvents.
Formation, Stability, and Film Forming Properties."

by

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Abstract

Palladium atoms in cold acetone, ethanol, and other organic solvents cluster to form living colloidal particles. The Pd colloids are stable for months at room temperature in acetone, and their particle sizes (about 8 nm) vary slightly according to solvent:Pd ratio, and warming procedures. The particles are stabilized by both steric stabilization (solvation) and by incorporation of negative charge. They are "living" in the sense that production of larger particles and films can be accomplished simply by solvent removal. The Pd films formed at room temperature by solvent evaporation have semiconductor properties (rather than metal like conductivity) due to the incorporation of substantial portions of organic solvent (and small amounts of solvent fragments). Upon heat treatment the films become smoother, give up organic solvent, and resistivity decreases.

These are the first examples of non-aqueous Pd colloids, and the first examples of film formation from such colloidal solutions. (Key words)

A-1

Living Colloidal Palladium in Non-Aqueous Solvents. Formation,

Stability, and Film Forming Properties. Clustering of Metal

Atoms in Organic Media 14.

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Abstract

Palladium atoms in cold acetone, ethanol, and other organic solvents cluster to form living colloidal particles. The Pd colloids are stable for months at room temperature in acetone, and their particle sizes (about 8 nm) vary slightly according to solvent:Pd ratio, and warming procedures. The particles are stabilized by both steric stabilization (solvation) and by incorporation of negative charge. They are "living" in the sense that production of larger particles and films can be accomplished simply by solvent removal. The Pd films formed at room temperature by solvent evaporation have semiconductor properties (rather than metal like conductivity) due to the incorporation of substantial portions of organic solvent (and small amounts of solvent fragments). Upon heat treatment the films become smoother, give up organic solvent, and resistivity decreases.

These are the first examples of non-aqueous Pd colloids, and the first examples of film formation from such colloidal solutions.

Introduction and Background

Although colloidal metal particles in aqueous media are well known[3], preparations in non-aqueous media have been hampered by low stability of the colloids presumably due to ineffective stabilization mechanisms (low solvent dielectric constant, low viscosity, etc.), and preparative methods. However, we have recently reported a successful, new approach to the preparation of stable metal colloids in non-aqueous media based on the process of atom clustering at low temperature.[4] This process appears to be very wide in scope and the resultant colloidal particles are free of interfering ions and impurities usually present in aqueous preparations. In addition, they are "living colloids" since particle growth to films occurs under very mild conditions, and can be induced simply by solvent evaporation. In this paper we report details on non-aqueous palladium colloids.

Palladium and Platinum Colloids

Some years ago Rampino and Nord[5] prepared Pd and Pt catalysts in which synthetic high polymers were used as protective coatings (steric stabilization of colloidal particles).[6] Palladium-methyl methacrylate (MMA) was prepared by adding glacial acetic acid to MMA followed by addition of palladium chloride solutions. Similarly Pd-polyvinyl alcohol (PVA) was prepared and shown to be a very efficient hydrogenation catalyst. The Pd-PVA and Pt-PVA catalysts were equally active in acid, neutral, and alkaline media.

Stable aqueous Pt sols (colloidal particles) have been prepared by the citrate reduction of chloroplatinic acid.[7] It was found that the Pt particle size and the extent of reduction of the chloride salt increased with temperature. These Pt sols with particle diameters in the range of 1.5

- 4 nm exhibited great resistance to coagulation by electrolytes such as LiCl, NaCl, KCl, CsCl, MgCl$_2$, SrCl$_2$, CaCl$_2$, BaCl$_2$ and AlCl$_3$. It was also found that H$_2$ treatment caused particle growth to about 5 nm.

Colloid Stabilization

There are two principle mechanisms for stabilization of metallic colloids: (1) electrostatic; colloidal particle charging due to adsorption of innocent ions in the solution[8] (such as chloride ion), and (2) steric; solvent ligation or polymer adsorption or ligation. Addition of polymers to aqueous or non-aqueous colloid solutions can have significant stabilization effects due to steric features or due to depletion stabilization (rejection of polymer molecules from the interparticle region is not favored thermodynamically due in large part to proper solvent choice).[6,9,10] Polymer stabilization is very important industrially for such products as paints, inks, food emulsions, oil recovery, waste treatment, etc.[6,11,12] Biological systems are also affected in similar ways, such as milk and blood.[6]

In our system, where only metal particles and solvent are present (no ions and no polymers) the question of stabilization mechanism is quite intriguing, and will be discussed.

Results

The following scheme was used to prepare stable Pd/solvent colloidal solutions[13] with acetone as an example:

$$Pd\ atoms\ +\ CH_3\overset{O}{C}CH_3$$

77K
cocondense

$$Pd(CH_3\overset{O}{C}CH_3)_x$$
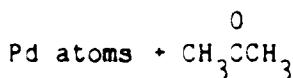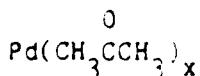
Stage I

Slow warm up (1.5 hr)
to room temperature

$$(Pd)_n(CH_3\overset{O}{C}CH_3)_y$$
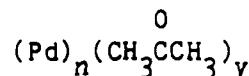
Stage II

The colloidal particles obtained at Stage II were air stable and remained in solution indefinitely. A series of black colloidal solutions using different concentrations and slightly different procedures was prepared (Table 1). In order to learn more about these particles several measurements and studies were carried out:

(1) Electrophoresis

Generally aqueous metallic colloidal particles carry some negative charge,[8] and the rate of migration of these particles to a positive pole can be determined, which is the electrophoretic mobility (μ_E). For our 0.0308M and 0.0360M Pd-acetone solutions (8 nm particle) the rate of migration was reproducibly 3.3 mm/h. (see Table 1)

$$\text{Field Strength} = X = \frac{E}{1} = \frac{-12.67V}{23.5\ cm} = -0.539V/cm$$

$$\text{Velocity} = v = \frac{3.3mm}{3600\ s} = 9.17 \times 10^{-4}\ mm/s \text{ (for 8 nm particles)}$$
$$= 9.17 \times 10^{-5}\ cm/s$$

$$\mu_E = \frac{v}{X} = \frac{9.17 \times 10^{-5}\ cm/sec}{-0.539\ V/cm} = -17.0 \times 10^{-5}\ cm^2/V\text{-}sec$$
$$= -1.7 \times 10^{-8}\ m^2/V\text{-}sec$$

This value is similar to those reported for a variety of aqueous colloidal particles, e.g. colloidal gold = 30-40 x 10^{-5} (<100 nm particle diamater) colloidal platinum 20 x 10^{-5} (<100 nm), colloidal lead 12 x 10^{-5} (<100 nm), and oil droplets = 32 x 10^{-5} (2000 nm).[14,15] It is interesting to note the similarities of these values regardless of particle size, which suggests that larger particles possess much higher overall charge.

The Debye-Huckel approximation may be used to express the charge density as a function of potential if it is low.[16] The potential at the surface of the particle is defined as the zeta potential ζ.

The zeta potential can be calculated according to the convention of Hunter[17] and the Huckel equation:

$$\mu_E = 4\Pi\epsilon_o D\zeta/6\Pi\eta = 2\epsilon_o D\zeta/3\eta$$

where for acetone D = dielectric constant = 20.7

ϵ_o = permittivity = 8.854×10^{-12} F/m

η = solvent viscosity = 3.16×10^{-4} N-sec/m^2

$\mu_E = ((2/3)(8.854 \times 10^{-12})(20.7)\zeta)/3.16 \times 10^{-4}$

$\zeta = 2.58 \times 10^6 \mu_E$

$\zeta = (-1.7 \times 10^{-8})(2.58 \times 10^6)$

$\zeta = -4.39 \times 10^{-2}$ volts = -44 mvolts

This value compares well with those reported for a variety of aqueous sols, ie. 18 to 58 millivolts.[14] Such comparisons are tenuous, however, since the equations derived and the data accumulated in the literature are for aqueous systems. Much more work with non-aqueous media is needed.

It is interesting to note that when a gold ground wire or wire connected to either pole of a 12 V battery was immersed in the solution as colloid formation took place, more highly charged particles resulted, and zeta potentials of greater than 100 mV were calculated (Table 6 compares rates of migration).

(2) Flocculation

Various electrolytes were added to the Pd/acetone colloidal solutions in order to induce flocculation.[8] Three solutions 0.01M of NaI, CaI_2 and $AlBr_3$ were prepared in acetone respectively. Addition of NaI

solution to Pd/acetone colloid 0.0175M in a ratio of Na:Pd=1:1 caused flocculation to begin in 5 min at room temperature. Addition of CaI_2 solution to the same colloid in the same ratio caused flocculation to begin in 3 min. Finally, addition of $AlBr_3$ solution to the colloid in the same ratio of Na:Pd induced flocculation in 2 min. This result is in agreement with data reported by Furlong[7] in which high valent cations induced flocculation faster than monovalent cations. Addition of water to the colloid induced flocculation only after 120 h at room temperature.

(3) **pH Measurements**

No evidence for increased acidity or basicity was obtained by measuring pH of the colloidal solutions. The same values for pure acetone were observed (7.7 pH units).

(4) **Other Solvents**

Ethanol, isopropyl alcohol, and acetone-isopropyl alcohol mixtures all worked very well as solvents for Pd colloidal formation and stabilization. Ethanol allowed slow flocculation after about 24 hours although with the other solvents indefinite colloid stability was observed (room temperature).

Thin Films

Stage II can be converted to Stages III and IV:

$$(Pd)_n(CH_3\overset{O}{C}CH_3)_y$$
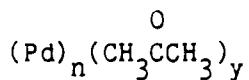
Stage II

solvent evaporation

Metallic like Pd Film

Stage III

Heat

Metal Film

Stage IV

Stage III was prepared by slowly dripping the colloidal solution onto a substrate. Solvent evaporation was speeded by applying vacuum, N_2 gas flow, or by using a warm substrate. Stage III was also prepared in uniform thin films by spraying the solution as an aerosol. Stage IV was obtained by heating Stage III under vacuum or in a stream of N_2. Films from Stages III and IV were analyzed and characterized in a variety of ways as follows:

(1) Elemental Analyses and Pyrolyses

Stage III after drying at 10^{-3} Torr for 3 hours still contained substantial portions of carbon and hydrogen (Table 2). Vacuum pyrolysis at 500 °C to reach Stage IV caused the evolution of mainly acetone along with some carbon dioxide.

A more detailed pyrolysis study using GC-MS was carried out at temperatures of 25, 100, 200, and 350 °C. Table 3 indicates the products that were successively evolved. At the lower temperatures acetone was the main product while at higher temperatures butenes, propene, and other similar products were evolved.

(2) IR Studies

Infra red analysis of the Stage III film indicated the presence of only adsorbed acetone. Strongest absorption was at 2980 and 1740 cm^{-1} similar to pure acetone.

(3) SEM and TEM Studies

Dilute solutions were dripped onto carbon coated copper grids so that acetone evaporation left isolated particles. According to transmission

electron microscopy (TEM) the particles were spherical and have a tendency to link together (Figures 1 and 2).

Scanning electron microscopy (SEM) showed that the film formed by acetone evaporation was made up of a series of strands or chains of colloidal Pd particles that were intertwined. Upon heating these strands collapsed to a more uniform film (Figure 3).

(4) Resistivity

Films of different thickness (2.8-65 μm) were prepared by dripping the colloidal solutions on a glass plate. The values of thickness and resistance are summarized on Table 4. After heating the films, resistivity decreased.

(5) Reaction with $(C_6H_5)_2P(C_2H_5)$

After solvent evaporation at room temperature the resultant Pd film (25 mg) was treated with excess $(C_6H_5)_2P(C_2H_5)$ under nitrogen. After stirring for 48h under nitrogen the volatiles were removed, separated, and identified. Besides excess phosphine, only acetone (0.39 mg or 6.8×10^{-3} mmole) was collected. This corresponds to about 1.6% of the total weight of the sample.

Discussion

The novel features regarding these materials are that the particles are stable toward flocculation in non-aqueous solvents, and they are "living colloids" in that the particles grow to films under very mild, controlled conditions. We will now consider what is known about formation and stabilization mechanisms for these materials.

The growth of colloidal particles from solvated atoms is in competition with the reaction of the atoms and growing particles with the solvent medium.[18] As would be expected, one process being favored over the other depends on what metal and what solvent are interacting. In the case of non-polar solvents and reactive metals, such as Fe, Co, or Ni, extensive bond breaking reactions have been observed (eg. Ni with pentane).[19] However, more polar solvents with better ligating properties tend to solvate the metal species with less bond breaking of the solvent molecules. In other words, solvent <u>molecules</u> complex with the metal species rather than <u>fragments</u> of the solvent.

In the case of Pd-acetone colloidal particles, we have found no evidence for adsorbed species other than acetone itself. Thus, vacuum treatment of Stage III at room temperature and 100°C yielded only acetone as a volatile product. At higher temperatures products were evolved that were probably formed from catalytic/pyrolytic decomposition of acetone. In addition, ligand displacement by excess $(C_6H_5)_2P(C_2H_5)$ yielded only acetone, and IR studies suggest that the only displaceable organic material is acetone itself. But note that it is quite strongly coordinated requiring vacuum and warming for just partial removal. A strong solvation mode is apparently important. On the metal cluster surface a variety of binding schemes may be operational, as suggested by Weinberg and Templeton[20] for acetone on a Ru(001) surface:

$$O = C \begin{matrix} CH_3 \\ CH_3 \end{matrix} \qquad O \quad C \begin{matrix} CH_3 \\ CH_3 \end{matrix} \qquad O \quad C \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

$$M \qquad\qquad\qquad M \qquad\qquad\qquad M - M$$

95K

$$M - C - CH_3 \atop \displaystyle CH_3$$
$$O - M$$
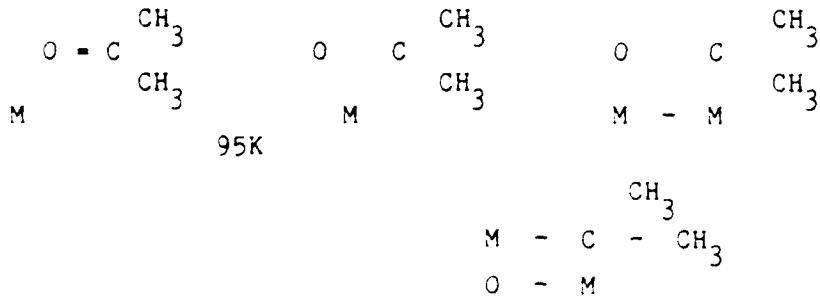
As our Pd particles grow to hundreds of atoms, solvent molecules would be incorporated within the particles and on the outside. As growth continues, some solvent molecules must be displaced by incoming atoms and smaller metal particles. Eventually the particle growth stops. At what point it stops (ultimate particle size) depends on initial metal concentration in the matrix, and matrix warmup procedure.

(1) Metal Concentration

Initial metal concentration can affect colloid particle size in a kinetic way, since it is unlikely particle growth is reversible under such conditions.[21] Once a Pd-Pd bond is formed, it does not break. Therefore, in a dilute solution of atoms, the frequency of encounters will be lower. As the metal atom-solvent matrix warms and the atoms become mobile and the forming particle becomes mobile, it is the number of encounters that occur during the period before particle stabilization that is important. And if metal concentration becomes too high, particle size becomes too large, causing precipitation. Similar behavior has been encountered for gold colloids in acetone[21]. Interestingly, however, gold particle size could be more easily controlled by concentration effects.[21] With palladium we invariably obtained particle sizes of 6-12 nm. Low concentrations of Pd still yielded 6-8 nm particles, and high concentrations of Pd yielded 8-12 nm particles plus much larger particles that precipitated. Thus, there is a distinct preference for 8 nm average particle size for Pd in acetone as well as for Pd in ethanol. We do not fully understand this selectivity yet, although particle stabilization must be the key, as discussed below.

(2) Particle Stabilization

We believe particle growth stops because of two factors. The first comes under the heading of steric stabilization.[5] Solvent molecules must be

displaced and reordered on the surface of a Pd cluster if another cluster is to chemically bind to it. As the particles (clusters) become more massive the kinetic energy goes down and perhaps the energy requirement for solvent displacement/reordering becomes large compared to the kinetic energy of the sluggish larger particles.

A second mode of stabilization is electronic in nature. Electrophoresis experiments clearly show that the Pd particles bear negative charge. Although it is difficult to determine accurately the number of negative charges each particle possesses (formulas derived for such calculations are based on aqueous systems) it is clear that these negatively charged particles will repell each other and therefore aid their stabilization. Zeta potentials are indicative of substantial electronic stabilization.

How is this negative charge acquired? One possibility is that free radicals are involved, perhaps formed by pyrolytic decomposition of small amounts of acetone on the hot metal vaporization source, or by reactions of acetone with metal atoms. A number of radiolysis studies of metal colloids in water-acetone solutions indicate that organic radicals do transfer electrons to the particles which act as electron reservoirs and can behave as catalysts for water reduction).[22,23]

$$(CH_3)_2\dot{C}OH + (Ag)_m \rightarrow (CH_3)_2 C^+-OH + Ag_m^-$$

$$CH_3COCH_3 + H^+ + Ag_m^-$$
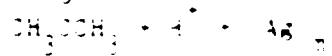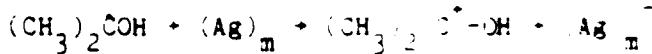
If free radicals were involved in our system, the formation of ... solution would be expected. However, we have found ...

solutions nor have we found any radical recombination products that might be expected. Therefore, we do not believe free radicals are important in the generation of negatively charged metal particles in our system.

A second possibility is that the electron affinity of the particles may allow them to acquire electrons from the reaction vessel walls, electrodes, and solvent medium. Such a process would help explain the need for a slow warmup procedure in order to yield stable colloidal solutions since scavenging of electrons may be a slow process.

Actually this type of electrostatic charging of colloidal particles is not uncommon. Oil droplets for example scavange electrons from aqueous solution.[14]

If scavenging occurs during the warmup period we reasoned that by inserting a gold ground wire into the solution during colloid formation some change would be realized. Indeed, using this procedure the resulting Pd particles became more highly negatively charged according to electrophoresis studies Table 1. The next step was to place a wire attached to the negative pole of a 12 Volt battery into the solution during colloid formation. In this case electrophoretic behavior changed markedly and measurements were impossible due to uncontrolled mixing. A last case was to attach the wire to the positive pole of the battery, and this again caused a significant change in the behavior of the colloid. The migration rate was the highest measured Table 1 and the colloid was very stable. Since a circuit was not complete, either pole of the battery simply served as a reservoir of electrons and more electrons were available yielding more negatively charged particles.

Based on the above observations we believe particle stabilization occurs slowly during the warmup period by steric effects solvation and by

electronic effects where the growing particles develope and possess a sufficiently high electron affinity that electron scavenging from the reactor environment is possible. This scavenging can be affected by the presence of electron sources, and electrophoretic mobilities increased. Such experimental manipulations hold promise for controlling electrophoretic mobilities and perhaps particle size.

Further support for this electronic stabilization mechanism is found in our studies of electrolyte additions. It is known that electrolytes added to aqueous metal colloids aid the breakdown of the charged double layer, which in turn allows particle flocculation.[8,14,15] Our studies with electrolytes yielded similar results. The electrolytes with the more highly charged cations caused flocculation more quickly ($Al^{3+} > Ca^{2+} > Na^+$). This is a classic case showing not only the existence of charged colloidal particles, but also that a charged double layer must exist.[14]

'2) Living Colloids → Films

From Table 2 it is evident that substantial portions of organic residue remain in the films after solvent stripping at room temperature. We found that the films were susceptible to oxidation, as might be expected, and oxygen (by difference) ranged as high as 25%. If care was taken to prevent oxidation an empirical formula of about $Pd_5C_2H_2O_2$ was determined. An average of all determinations indicated $Pd_9C_5H_7O_{11}$. After treatment at 500°C causing the evolution of some organic material, an average empirical formula of $Pd_4C_1O_3$ was determined.

Earlier discussion suggested that while in solution the colloidal particles are solvated by acetone, and other organic fragments were not detected. However, upon stripping of solvent it is obvious from the empirical formulas that acetone must be breaking up accompanied by some

oxidation. Some acetone is still present since it is the main volatile product evolved at 300°C (Table 3), and the only volatile product displaced by $(C_6H_5)_2P(C_2H_5)$. Since the remaining fragments must be very rich in carbon and oxygen, the formation of palladium carbides and palladium oxides is likely.

Electron microscopy studies show that the individual colloidal particles are spherical and have a tendency to link together in chains. The initial film appears to be made up of a network of Pd particle chains (Figure 2). Upon heating these chains collapse to a more uniform film (Figure 3).

Resistivities of these films are of interest. Table 4 lists values determined for 1 cm^2 films of varying thickness (0.2 - 60 μm). The initial films are conductive, but increase in conductivity after heating. They behave more like semiconductors than pure metals, and actually their resistivities are similar to those of doped organic polymers.[24]

Conclusions

Palladium atoms dispersed in excess acetone (or other solvents) begin to cluster upon warming. The properties of the resultant colloidal particles depend slightly on initial metal concentrations, warmup procedures, and the availability of electrons. During colloid formation the particles are stabilized by solvation effects and by electronic effects due to electron scavenging (the Pd particles behave as electron sinks). Upon solvent removal films of intertwined chains of spherical Pd colloidal particles (still containing organic residues) are formed. Upon heating these chains collapse to a uniform film with a decrease in resistivity. Some organic residue remains in the films.

Experimental Section

Preparation of a typical Pd-Acetone Colloid

The metal atom reactor has been described previously.[13,25] As a typical example, a W-Al$_2$O$_3$ crucible was charged with 0.80g Pd metal (one piece). Acetone (300 ml, dried over K$_2$CO$_3$ was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 1 x 10^{-4} Torr while the crucible was warmed to red heat. A liquid N$_2$ filled Dewar was placed around the vessel and Pd (0.5g) and acetone (189g) were codeposited over a 1.0 hr period. The matrix was a dark brown color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid N$_2$ Dewar for 1.5 hr..

Upon meltdown a black solution was obtained. After addition of nitrogen the solution was allowed to warm for another 0.5 hr to room temperature. The solution was syphoned out under N$_2$ into Schlenk ware. Based on Pd evaporated and acetone inlet the solution molarity could be calculated.

Effects of a Ground Wire and Battery Attached Wire

Several experiments were carried out where a gold wire was connected to an electrode inside the reactor so that it reached the bottom of the reactor. A copper wire was attached to the upper part of the electrode external to the vacuum chamber. This wire was either grounded or attached to the negative or positive pole of the 12V storage battery. Colloidal solutions obtained using these modifications did not show any marked changes in stability but electrophoretic mobilities increased.

Electrophoresis Experiments

The electrophoresis experiments were carried out by using a glass U-tube of 11.0 cm each with an stopcock on the base to connect a perpendicular glass tubing of 13 cm long and 35 cm hignt.[14,26] Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the

pole of a 12V battery. The acetone was placed in the U-tube and then the colloid solution added slowly through the side tube. The migration rate was determined based upon the average of the displacement in each side of the U-tube. A typical experiment was carried out for a period of 3 hr. at 25°C.

Electrolyte Additions

An study of flocculation times was carried out by using a 0.010M NaI solution. In a test tube 2 ml of colloidal solution (0.0175M) and 2 ml of NaI were added at room temperature (25°C). After 5 min. flocculation of the colloid was observed.

A solution of 0.010 M CaI_2 in acetone was also prepared. Using the same ratio as before, flocculation of the colloid began after 3 min. Finally, a 0.010M $AlBr_3$ acetone was prepared. Addition to the colloid in the same amount as before induced flocculation after 1 min at room temperature. Complete flocculation was observed after 10, 8 and 7 min respectively.

In other experiments water was added to the colloid solution and after 120 hr. flocculation was observed.

GC-MS Experiments

GC-MS pyrolysis was carried out using a Porapak Q column 6-ft (flow rate 35 ml/min) attached to a Finnigin 4000 quadrupole GC-MS. The sample was placed in a stainless steel tube 10 cm long connected to a 4 way valve. One of the outlets was attached to a Porapak Q column interfaced with the M.S. The stainless steel tube containing a portion of Pd colloid film Stage III was placed in a furnace connected to a Variac provided with a digital quartz pyrometer to measure the temperature. Three pyrolysis were performed at 100, 200 and 350°C with the Pd-acetone film (from colloid 0.0521 M).

Addition of $(C_6H_5)_2P(C_2H_5)$

A Pd film was prepared by evaporating the solvent from a 0.035M colloid solution. A 25mg sample of the film was treated with 1.5 ml of $(C_6H_5)_2$ $P(C_2H_5)$ (5.6 mmole) under nitrogen atmosphere. After 48 h at room temperature under stirring the dark solution became lighter. The volatiles were pumped out through 263 and 77 K traps. The 77 K trap contained only acetone (0.39 mg or 6.8×10^{-3} mmole) identified by gas phase IR.

SEM and TEM Studies

Electron micrographs were obtained on a JEOL, TEMSCAN -- 100 CX11 combined electron microscope and a HITACHI HV-11B (TEM) operated at 2×10^5 magnification. The specimens for TEM were obtained by placing a drop of the colloid solution on a copper grid coated by a carbon film. The samples for SEM were placed between two copper grids one of which was coated by a carbon film.

Resistivity Studies

Films of different thickness (02.8-65 μm) were prepared by dripping the colloidal solutions on a glass plate edged with Silicon rubber adhesive resin. The acetone was allowed to evaporate. Resistivities were measured by scrapping the silicon rubber away from the edges of the film, which was then trimmed to rectangular shape. It was then connected to electrodes on each end by vapor depositing an opaque film of aluminum or copper. To get a reliable contact on aluminum, it was necessary to apply a spot of silver paint over the aluminum. This was not necessary with copper electrodes. The resistance of each sample was measured with a Digital Multimeter KEITLEY 178 Model. The vapor depositions were carried out using a Metal Evaporator VEECO Model VS-90. The values of thickness and resistance are summarized on Table 4.

Solubility Studies

The solubility of the Pd-acetone film (0.0236 M) was tested using the following solvents: acetone, ethanol, THF, DMSO, benzene, toluene and pentane. The films are completely insoluble after 24 hrs in contact under stirring at 25 °C.

Infra Red Studies

Infrared spectra were recorded in a Perkin Elmer PE-1330 infrared spectrometer. IR studies of the metal films using either KBr pellets or Fluorolube yielded only evidence for νC-H (2980 cm^{-1}) and νCO (1740 cm^{-1}) showing the same shape as the acetone standard.

Acknowledgements

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Table 1. Electrophoresis Studies of Pd-Acetone Colloids

Solvent	[M]	Rate of Migration (mm/hr)	Particle Size (Average) (nm)
Acetone	0.0308	3.3	8
Acetone	0.0360	3.3	8
Acetone	0.0038[a]	8.0	8
Acetone	0.0170[a]	8.0	6
Acetone	0.0138[b]	8.3	8
Acetone	0.0228[a]	6.0	6
Acetone	0.0200	--[c]	8
Acetone	0.0096[d]	10.0	8
Ethanol	0.0416	3.0	8

a. Au wire connected to left electrode on bottom reactor, also Cu wire connected to ground.

b. A Pd-Au bimetallic colloid

c. It was impossible to carry out electrophoresis since the colloid, mixed with the solvent. In this experiment during the warm up the left electrode was connected to the negative pole of a battery.

d. During the warm up the left electrode was connected to the positive pole of a battery.

Table 2. Pd films prepared from Colloid Solutions with Organic Solvents

Solvent	[M] range	%Pd	%C	%H[a]	Colloid particle size (nm)
Acetone	0.0236-0.0588[b]	79.70	4.90	0.58	10-14
Acetone	0.0588 (500°C)[c]	88.47	2.30	0.07	-
Ethanol	0.0178-0.0416	73.43	4.40	0.85	unresolved
Acetone	0.0138[d]	25.35(55.29)	5.45	0.77	8
THF	0.0148	79.70	3.30	0.56	6
Isopropenol	0.0108	79.90	6.00	1.10	6

a. Microanalyses were obtained from Galbraith Laboratories

b. Average from several colloids within this range of concentrations.

c. Film after heating at 500°C. The %C varied from 0.4 to 2.5 over several samples. The %H varied from 0.03 to 0.07, while the %Pd varied from 88.3 to 88.5.

d. (Au-Pd)-acetone colloid, in parenthesis %Au.

Table 3. Products Evolved Upon Heating Films Derived From Pd-Acetone Colloidal Solutions[a]

Temp. (°C)	Products (relative %)
100	H_2O (25.6), CO (41.2), CO_2 (11.8), $(CH_3)_2C=O$ (13.2)
200	H_2C (8.4), CO (27.7), CO_2 (2.3), $CH_3CH=CHCH_3$ (24.7), $(CH_3)_2C=O$ (36.5)
350	H_2O (5.9), CO (21.2), CO_2 (3.1), C_3H_6 (2.7), C_4H_2 (0.3), C_4H_4 (0.2), C_2H_5OH (0.7), $CH_3CH=CHCH_3$ (28.8), $(CH_3)_2C=O$ (37.5)

a. The film was obtained by stripping the acetone solvent under vacuum at room temperature for 3 hr. Initial concentration of the colloid was 0.0521M.

Table 4. Resistivities of Films Stages III and IV ... ... Colloids.

[M] Solution	Resistance Ω·cm²	Thickness	Resistivity
0.0165	71-93[a]		
0.0165[b]	43		
0.0298	83-107		
0.0228	49-109		
0.0138[c]	380		
Pd film[d]	357		
Pd bulk[e]			
Cis[CH(AsF$_5$)$_{0.14}$][f]	n		
TTF·TCNQ[g]	n		

a. Values varied within this range by measuring resistivities of different sections of the film.

b. The film was heated for 1 h at 200°C, then resistance was measured.

c. A Pd-Au bimetallic colloid solution.

d. A pure Pd film for comparison, prepared ... vapor.

e. Handbook of Chemistry, ...

f. Polyacetylene, doped with AsF$_5$.

g. Measured on a single crystal in the direction of ...

h. Not reported.

Figure Legends

Figure 1. Transmission Electron Micrograph of Particles Derived from a Pd-Acetone Colloid Very Dilute Solution 2.5×10^5 magnification.

Figure 2. Scanning Electron Micrograph of Film Stage III Derived from a Pd-Acetone Colloid 1.1×10^5 magnification.

Figure 3. Scanning Electron Micrographs of Films Stage IV Derived From a Pd-Acetone Colloid.
    a   After heating at 180°C 5×10^4 magnification.
    b   After heating at 600°C 1×10^4 magnification.

40 nm
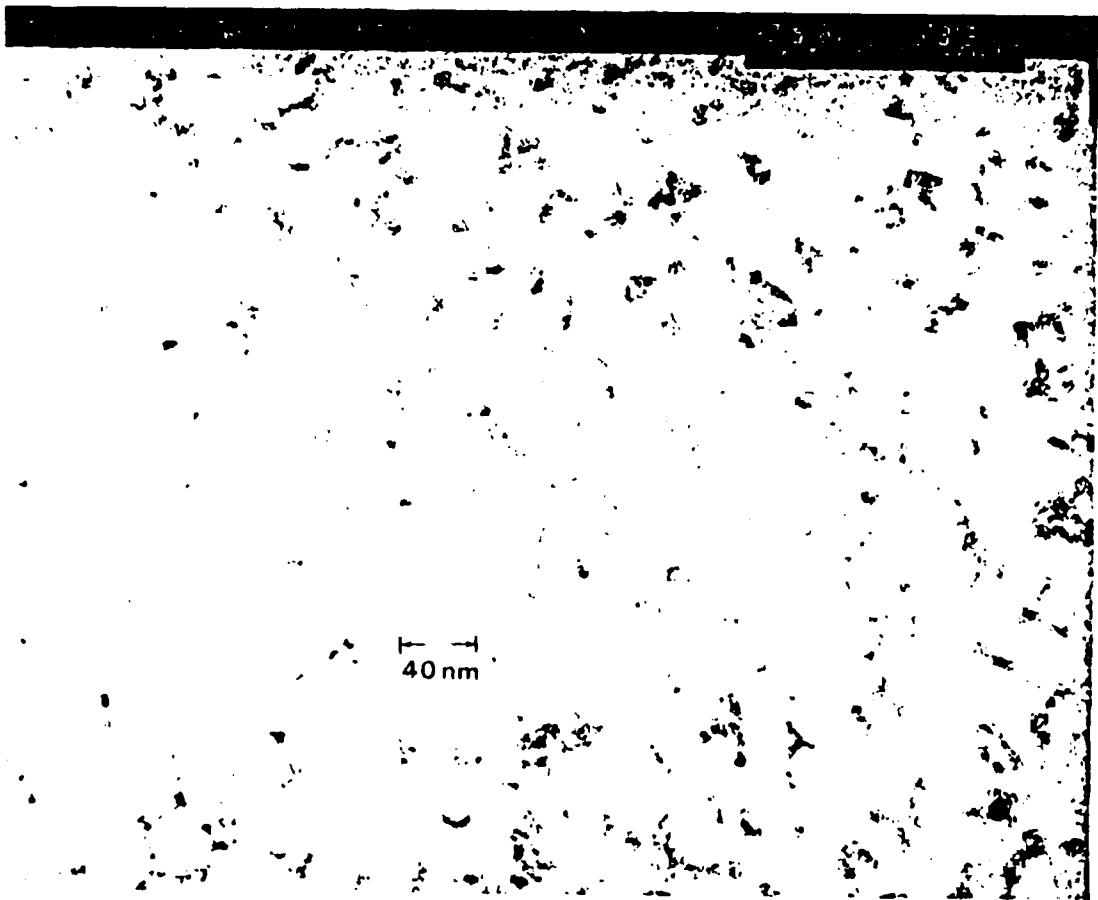
Figure 1

Figure 2

GC-004F   x 10⁵

CC 004F(180°C)   x 3000

Figure 3 (A)

GC-004F (500°C)   x 1.5

Figure 3 (B)

END

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